Optical Method of Determining the Concentration
of Atoms and Molecules in the Ground State

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The phenomenon of anomalous dispersion has been used quite fruitfully by Rozhdestvensky[1] and his pupils, who evolved the famous "Hacken-Methode." This method makes it possible to measure with great accuracy considerable optical densities, but involves quite formidable work on spectrograms. The theory of the "Hacken-Methode" for determining the optical density of molecular substances has not yet been evolved, and so far its use is limited to the study of atomic vapors of certain metals.

The method we are suggesting can in many cases simplify measuring and enable us to use the phenomenon of anomalous dispersion to study the processes occurring in substances with a molecular structure. The method consists of the following. We know that when a layer of a substance is introduced into one branch of the Rozhdestvensky interferometer crossed with a spectrograph and when light is transmitted through an optical system from the source of a continuous spectrum, then dispersion curves are observed in the spectrograph near the absorption lines or bands. When a layer of the same substance and of equal thickness is introduced into the other branch, then the interference fringes near the absorption lines will straighten out, since the optical lengths of the paths traversed by the two interfering pencils will be equal for all wavelengths. Let us now assume that a certain process, accompanied by a change in the concentration of absorbing particles, takes place in the first layer. Then the interference fringes will be distorted near the absorption lines or bands. The interference fringes can be straightened again by a corresponding change in the thickness of the second layer. Here, the layer acts as a compensator. It is evident that a relative change in the concentration of absorbing particles caused by the process in the first layer will be equal to the relative change in thickness of the compensator.

Thus the determination of the change in the concentration of absorbing particles in the given layer of the substance can be reduced to observing the interference pattern and to measuring the linear dimensions of the compensator.

In many cases it may be more convenient to change the density of the substance in the compensator than to change the dimensions of the compensator. Thus in studying solutions one can change the concentration of the molecules of a given kind in a solution. When a substance is studied in a vapor state, the compensation can be made by changing the density of the vapor. If a substance consists of particles of different kinds, their concentrations can be determined selectively. The proposed method can obviously be used for studying

substances whose absorption lines and bands are in a spectrum region accessible to visual observation or photographing; it cannot be used to study processes causing the displacement of the bands over the spectrum.

We have used the compensation method to determine the concentration of normal cesium atoms in the positive column of a discharge. (M. A. Prokofyeva took part in the experiment.) We introduced a compensator (a cell of a certain length filled with cesium vapors) into one branch of the interferometer. A discharge tube was introduced into the other branch. The density of the vapor in the tube, which was a certain number of times greater than that in the compensator, was established before the discharge. Dispersion curves of a certain slope (Fig. 1, 1) were observed near the absorption lines. Then the discharge current was switched on, the other conditions remaining the same. This caused the slope of the curves to diminish (Fig. 1, 2). The slope of the curves diminished constantly with the increase in the discharge current; and when the current reached a certain value the fringes were completely straightened (Fig. 1, 3). Further increase in the strength of the discharge current caused the fringes to curve in the opposite direction from the original curvature (Fig. 1, 4). The changes in the concentration of normal atoms caused by discharge were determined independently by the "Hacken-Methode" and the compensation method. The results coincided within the limits of accuracy and also agreed with our previous measurements.[2]
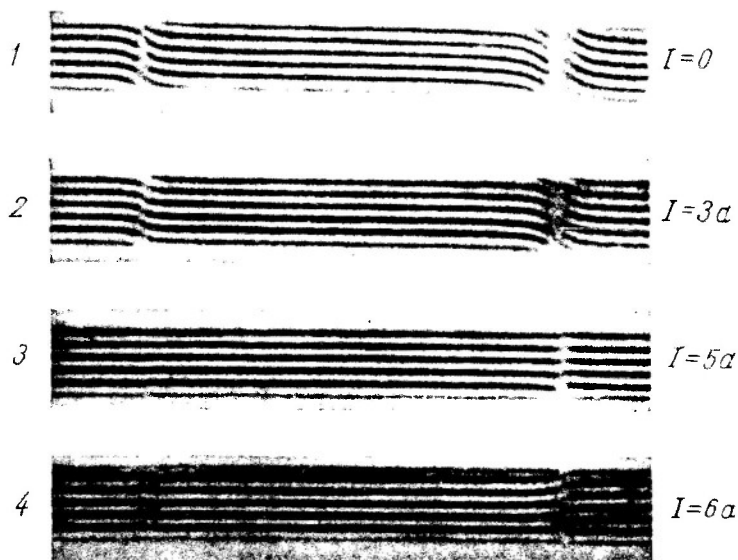

Fig. 1.

The slight distortion of the fringes near the absorption lines in the lower part of Fig. 1, 3 is due to the fact that the axes of the compensator and of the discharge tubes are not quite parallel.

Fig. 1 shows the reproductions of the spectrograms obtained in the region of the second doublet of the principal series of cesium ($\lambda\lambda$ 4555 and 4593 A). Simultaneously, we took photographs of the region of the first doublet of cesium ($\lambda\lambda$ 8943 and 8521 A). We found that the fringes are straightened simultaneously near both components of each of the doublets and, within the limits of accuracy, near the lines of various doublets. Hence, without measuring, one can rapidly conclude that the ratio of the f values within the doublet does not change and that, moreover, the absolute values of the f

values also remain constant under our discharge conditions. The straightening of the interference fringes also suggests that the shape of the dispersion curve of the excited vapor does not change.

The accuracy of the method is determined basically by the difference which can still be perceived experimentally in the concentration of the absorbing particles in the volume under study and in the compensator. It is quite simple to estimate this difference. When the interference maximum is displaced by a half-fringe from the straight line, it is already quite noticeable, and it will be even more noticeable when from the opposite sides of the absorption line the maxima move in opposite directions. The displacement of the maximum by a half-fringe, as can easily be seen, will occur when the difference between the optical lengths of the compensator and the column is $\lambda/2$. Using Sellmeier's formula for an isolated spectral line, the equation of the optical lengths of the compensator L_1 and of the object under study L_2 can be written as

$$
\begin{aligned}
L_1 &= \frac{e^2}{4\pi\,mc^2}\,\frac{\lambda_k^3}{\lambda_k - \lambda_0}\,N_1 f l_1 + l_1, \\[2mm]
L_2 &= \frac{e^2}{4\pi\,mc^2}\,\frac{\lambda_k^3}{\lambda_k - \lambda_0}\,N_2 f l_2 + l_2.
\end{aligned}
\tag{1}
$$

The factor $e^2/4\pi mc^2$ contains the known constants.

We shall take the difference between these lengths and set it equal to $\lambda/2$, assuming for simplicity that the lengths of the compensator (l_1) and of the column under study (l_2) are equal: $l_1 = l_2 = l$. Then, for the difference in the concentrations $\Delta N = N_1 - N_2$, we obtain

$$
\Delta N = \frac{2\pi\,mc^2}{e^2}\,\frac{1}{fl}\,\frac{\lambda_k - \lambda_0}{\lambda_k^2}\,.
$$

Here λ_0 is the wavelength of the absorption line, λ_k the wavelength corresponding to the displacement of the maximum by a half-fringe.

It appears from the expression (3) [sic] that the minimum difference in the concentrations of the atoms in the column under study and in the compensator that can still be noticed will be smaller if the factor $(\lambda_k - \lambda_0)$ is smaller, i.e., the closer the observation is to the absorption line.

When we work by the "Hacken-Methode," one of the pencils, as it passes through the absorbing layer, becomes considerably weaker in the spectral region near the absorption line, whereas the second pencil passes without weakening. As a result, it is impossible to observe the interference in the vicinity of the absorption line. In the compensation method, on the other hand, the intensity of both pencils is weakened identically over the entire spectrum. Therefore an interference picture can be obtained in immediate proximity to the absorption line. This ensures the high accuracy and sensitivity of the method.

Calculations show that the difference in the concentrations of atoms in the compensator and in the discharge column corresponding to Fig. 1, 3, does not exceed $\Delta N = 10^{12}$ cm^{-3}, which is about 0.1 percent of the measured concentration of atoms.

In conclusion, I wish to thank Corresponding Member of the USSR Academy of Science S. E. Frish [Frisch] for his careful guidance of our work.

[1]D. S. Rozhedestvensky, *Anomalnaya dispersia v parakh natria* [Anomalous Dispersion in Sodium Vapors] (St. Petersburg, 1912); *Prostye sootnoshenia v spektrakh shchelochnykh metallov* [Simple Relations in Spectra of Alkali Metals] (Petrograd, 1915); *Raboty po anomalnoi dispersii v parakh metallov* [Works on Anomalous Dispersion in Metal Vapors], 1951.

[2]A. M. Shukhtin, Doklady Akad. Nauk SSSR, **82**, No. 1, 41 (1952).